Magee Scientific Aethalometer®

Optical Transmission Analysis of NIST Reference Material 8785 and Neutral Density Filters

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Berkeley, Ljubljana, July 2014

Magee Scientific Optical Transmissometer

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Optical Transmission Analysis of NIST Reference Material 8785 and Neutral Density Filters for calibration and validation of the Magee Scientific Aethalometer® and Magee Scientific Optical Transmissometer

The Optical Transmissometer is an instrument which measures the attenuation of light transmitted through a sample of aerosol collected on a filter, relative to a blank filter. In the great majority of cases, this optical attenuation is due to absorption by the 'Black Carbon' (BC) component of the aerosol. This attenuation may be converted to a surface mass loading density of BC (expressed, for example, in units of $\mu g/cm^2$) using a filter-specific Mass Absorption Coefficient. This provides a 'static' analysis of the BC content of a previously-collected sample.

The Aethalometer® is an instrument which performs a 'dynamic', real-time measurement of the concentration of Black Carbon ('BC') aerosols in a sampled air stream, by measuring the rate of increase in optical absorption of the aerosol deposit on a filter spot. The data output is expressed in units of [BC mass] per [volume of sampled air], for example $\mu g/m^3$.

The calibration of these methods is based upon the determination of the relationship between the optical measurement of Attenuation ('ATN'), and a measurement of the mass of a specified form of carbon in the sample. While the optical measurement may be referenced to traceable photometric standards, chemical determinations of carbon mass are method-dependent.

Neutral Density Filter Reproducibility Validation Process

The reproducibility of the optical attenuation method employed by the Aethalometer and Optical Transmissometer may be validated by the use of Neutral Density Filter Validation Kits for each instrument. These kits consist of elements of Neutral Density optical filter glass, with stable optical absorbances that may be referenced back to traceable photometric standards. These kits are used to verify that the optical performance of the instrument is constant with time, relative to its original manufacturing certification.

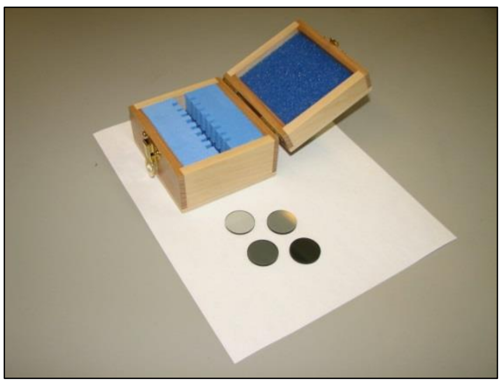

Figure 1:
Neutral Density Optical Filter Kit for OT21 Optical Transmissometer

Figure 2:
Neutral Density Optical Filter Kit for AE33 Aethalometer

The reproducibility validation procedure consists of inserting the Neutral Density elements into the optical path of the instrument, and recording the measured Optical Attenuation at the multiple analytical wavelengths. Each individual Neutral Density glass element is described by a "nominal" value of optical density at its time of manufacture. Due to variations in the manufacturing processes, the actual optical densities of the elements may differ from their nominal labels. However, the glass material is stable, and the Neutral Density validation process is based upon determining that the response of the instrument to the insertion of successive elements is stable and reproducible.

The 'ND Validation Process' is a reproducibility check, not a 'Calibration'

The Neutral Density Optical Filter validation process is not a 'Calibration' *per se*: it assures the user that the analytical performance of the instrument is reproducible and unchanged from its date of manufacture.

Optical Transmission Analysis of Standard Reference Materials

The absorption of light transmitted through a deposit of aerosol particles collected on a fibrous filter has been studied by many authors, for example Rosen and Novakov, (1983). This absorption can be attributed to the carbonaceous component of the aerosol (Rosen et al., 1978), in almost all atmospheres except those unusually affected by mineral or inorganic dusts (Hansen et al., 1993).

The relationship between the Optical Attenuation measurement and the thermal-chemical determination of the mass of certain fractions of carbon in the sample has been studied extensively and reported in the literature. The definitive original reference is Gundel et al., (1984). The procedures and results described therein serve to define Black Carbon, in terms of both chemical procedures and optical analysis. An example of more recent work is Ahmed et al., (2009). At increasing loadings, the optical attenuation measurement is subject to gradual saturation according to the well-known "filter loading effect" (Bond et al., 1999; Weingartner et al., 2003; Virkkula et al., 2007; Park et al., 2010).

The U.S. National Institute of Standards and Technology (NIST) created Standard Reference Material 8785, being uniform deposits of 'urban dust' collected on 37-mm. diameter quartz fiber filter disks, in varying densities. Each filter is weighed to report the total mass of 'urban dust' collected on the filter. Multiple analyses of the dust were performed to determine its content of "elemental" and "organic" carbon, as defined by instrument-specific thermal-optical analysis protocols (Klouda et al., 2005). The analyses using the 'IMPROVE' thermal-optical protocol showed that the 'EC' content of the 'urban dust' material was 11.1% ± 3.5% by mass.

We measured the Optical Attenuation of twelve SRM 8785 filters relative to a blank filter, using the OT21 Optical Transmissometer analyzing at a wavelength of 880 nm. The SRM 8785 filter samples were of identical composition: but contained different amounts of deposited material, determined gravimetrically and reported as total mass for each filter. The uncertainty over replicate optical measurements was ±1 ATN unit. ATN values ranged from 119 ±1 to 197 ±1, while the 'EC' surface loading density according to the NIST analysis data ranged from 7.8 $\mu g/cm^2$ ±2.6 $\mu g/cm^2$ to 29.8 $\mu g/cm^2$ ±9.4 $\mu g/cm^2$.

The optical analysis of NIST filters is a re-enactment of the original calibration which defines 'Black Carbon'

Measurement of the relationship between ATN and the surface loading density of 'EC' is an independent re-enactment of the original definitive calibration by Gundel et al. This process is accessible to present users through the ongoing availability of Standard Reference Material 8785 from the U.S. National Institute of Standards and Technology.

Measurement Results

The blue data points in Figure 3 show the relation between Optical Attenuation measured at 880 nm (ATN) versus the manufacturer's nominal 'label value' of optical density (specified at 550 nm) for the Neutral Density glass elements used in the Validation Kit. Since the validation process is based upon reproducibility rather than absolute values, the deviation of the points from perfect linear proportionality as suggested by the blue trend-line are unimportant.

The red data points show the relation between Optical Attenuation measured at 880 nm (ATN) versus the surface loading mass density of 'Elemental Carbon' (EC), for samples of NIST Standard Reference Material 8785.

The red trend-line shows a calculation of ATN versus EC using a Mass Absorption Coefficient ("$\boldsymbol{\sigma}$") of 16.6 m^2/g, with the saturation being represented by a loading parameter ("$\boldsymbol{k}$") of 0.0045 in the equation

$$ATN = (1-\exp(-\ \boldsymbol{k}\ B\ \boldsymbol{\sigma}))\ /\ \boldsymbol{k} \quad \text{(c.f. Gundel)}$$

This value (16.6 m^2/g, "$\boldsymbol{\sigma}$") for the Mass Absorption Coefficient (sometimes termed 'Specific Attenuation') has been used in the Aethalometer since the earliest production of instruments analyzing at 880 nm. The value of the loading compensation parameter ("$\boldsymbol{k}$") has been shown to be highly variable, depending on aerosol aging and composition (Drinovec et al., 2013). The value of 0.0045 used in the fit to the data shown in Figure 3 is within the central range of values expected for an aerosol of this nature.

These results show that the measurement of Optical Attenuation as used in the Optical Transmissometer and the Aethalometer may have their reproducibility validated by the use of stable Neutral Density optical elements; and that these results may be related to the thermal-chemical determination of 'Elemental Carbon' mass on Standard Reference Material samples available from the National Institute of Standards and Technology.

This relationship between a photometrically-traceable measurement of optical absorption; versus mass of carbon on a Standard Reference Material; serves to define the material named "Black Carbon", and to calibrate the response of the Aethalometer and the Optical Transmissometer.

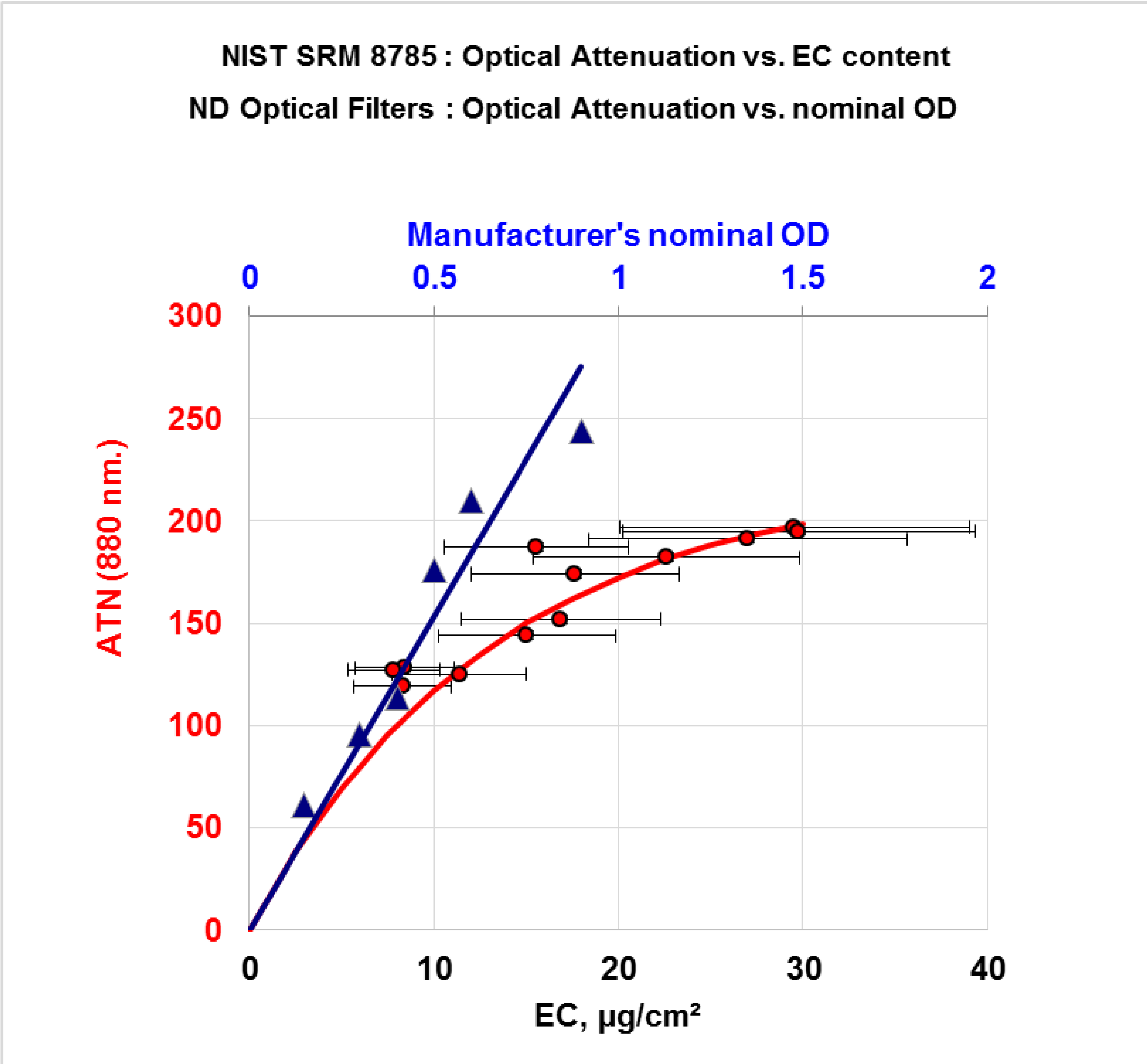

Figure 3: Analytical results from measurements.

Y-axis: Optical Attenuation measured at 880 nm using the Model OT21 Optical Transmissometer;
Upper X-axis: Nominal optical density (at 550 nm) of glass elements;
Lower X-axis: Elemental Carbon content of SRM 8785 filters, reported by NIST using the 'IMPROVE' thermal-optical analysis protocol.

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